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TRANSLATION

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THERMO-RETAINING MOISTURE PERMEABLE WATERPROOF CLOTH

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Application Date: September 8, 1987

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1. Title of Invention:

THERMO-RETAINING MOISTURE PERMEABLE WATERPROOF CLOTH

2. Claims:

Claim 1:

A thermo-retaining moisture permeable waterproof cloth that provides on the surface of the cloth a resin film which contains a ceramic particulate with an extreme infrared radiation ability.

Claim 2:

The thermo-retaining moisture permeable waterproof cloth mentioned in Claim 1 wherein the ceramic particulate is the transition metal carbide particulate of the fourth group of the periodic system.

Claim 3:

The thermo-retaining moisture permeable waterproof cloth mentioned in Claim 1 wherein the ceramic particulate is a transition metal carbide particulate (e.g.; silicon, boron, tantalum, etc.).

Claim 4:

The thermo-retaining moisture permeable waterproof cloth mentioned in either Claim 1, 2 or 3 wherein the resin is a synthetic polymer having a polyurethane as the main body.

3. Detail Explanation of the Invention:

[Industrial Application Field]

This invention concerns a moisture permeable waterproof cloth that has suitable heat retention properties needed for cold protection clothing and sport clothing.

[Prior Art Technology]

Up to this point, the creation of cold protection clothing and sport clothing involves the formation of a three-layer structure made by placing a cotton batting between the garment's main cloth and the lining. Heat retention properties are obtained by the thickness of the air layer of the cotton batting. However, such three-layer structured clothing has disadvantages. This is especially true when using the three-layer structured material for sport clothing which requires ease of movement. This is because such three-layered material is bulky, heavy and restricts freedom of movement. There have been recent efforts to resolve these problems by reducing the amount of the cotton batting or by not using any at all. The latter method uses either a heat retention effect (which reduces the escape of body heat from the surface of the cloth) by reflecting body heat at the surface of the cloth or by keeping and radiating body heat by using a moisture permeable waterproof cloth (which contains aluminum or carbon in the resin film) as the clothing's material.

[Problems Resolved by the Invention]

However, the moisture retaining waterproof cloth (which

contains the abovementioned aluminum or carbon in the resin film) does not provide sufficient heat retention until there is a large amount of aluminum or carbon in the resin film. As a result, other problems occur (e.g., a decline in the strength of the resin film, a decline of abrasion resistance and moisture permeability, etc.).

This invention has been achieved by considering such situations. The objective of this invention is to obtain a moisture permeable waterproof cloth that has excellent abrasion resistance and moisture permeability as well as good heat retention properties.

[Means for Resolving Problems]

The inventors have studied for some time how to achieve the objective. They discovered they were able to achieve the objective by adding a ceramic particulate having extreme infrared radiation ability into a moisture permeable waterproof resin film. This invention is the result.

More specifically, the crux of this invention is "a heat retaining moisture permeable waterproof cloth that has on its surface a resin film which contains a ceramic particulate having extreme infrared radiation ability."

This invention is explained in detail below.

Here the transition metal carbide of the fourth group of the periodic system (e.g., titanium, zirconium, hafnium, etc.), carbide (e.g., silicon, boron, tantalum, etc.), oxide (e.g.,

titanium, silicon, chrome, zirconium, iron, copper, etc.) and crystalline (e.g., mica, fluorite, calcite, etc.) are used as the ceramics having an extreme infrared radiation ability.

With regard to this invention, in order to give useful extreme infrared radiation ability to heat retention properties at a normal temperature range, it is preferable to mix them. The transition metal carbide of the fourth group of the periodic system which has a large far infrared radiation ability is especially preferred.

The particulate used in this invention is a fine powder which has been crushed to a grain degree of less than 20um, preferably less than 10um, and even more preferably less than 1um. If it is too large, various problems occur (e.g., streaks are generated over the surface of the resin film when the film is formed, the quality may decrease or the waterproof performance of its section may decrease, etc.).

In this invention, the synthetic polymer of a polyurethane resin main body is used to form the film.

The synthetic polymer used here is one which contains 50 - 100% of polyurethane resin (it certainly can be 100% polyurethane resin). Contained as another synthetic polymer can be one which contains less than 50% of a high polymer of polyacrylic acid, polyvinyl chloride, polystyrene, poly butadiene, poly amino acid, etc. Its shape can be either copolymer or blend. The synthetic polymer with a polyurethane resin as the main body which contains

a poly amino acid means a synthetic polymer with a poly amino acid urethane resin as the main body.

The polyurethane resin used in this invention is a mixture which is obtained by a reaction of a poly-isocyanate and a poly ole. A commonly known resin group and an aromatic poly-isocyanate are usable as the poly-isocyanate. For example, a hexamethylene di-iso cyanate, toluene diisocyanate, xylene diisocyanate and a reaction product of these and a polyalcohol can be used. A commonly known (e.g., polyether or polyester, etc.) which is used for common polyurethane resin manufacturing can be used as a poly ole. A reactant of polyalcohol (e.g., ethylene glycol, diethylene glycol or 1,4-butan diol, etc.) and a polybasic carboxylic acid adipic acid (e.g., oxalic acid or sebacic acid, etc.) can be used as the polyester. One [to which is added one or more than two kinds of alkylene oxide (e.g., ethylene oxide, propylene oxide, butylene oxide, etc.) to a polyalcohol (e.g., ethylene glycol, propylene glycol, etc.)] is usable as the polyether.

The preferred amount contained of a ceramic particulate having an extreme infrared radiation ability (contained in the resin film) is in the range of more than 0.1% by weight but less than 50% by weight (preferably more than 5% by weight but less than 25% by weight) to the weight of resin film. If the amount contained is less than 0.1% by weight, the objective heat retention properties cannot be obtained. If it exceeds 50% by weight, the film properties deteriorate as well as do the moisture

permeability and the waterproof performance.

The following method can be used as a method for adding the ceramic particulate (with extreme infrared radiation ability) to a resin film. The method coats and forms a film by adding a specific amount of ceramic particulate at the preparation of the resin solution after it is sufficiently mixed by a suitable agitator for the viscosity of the resin solution.

A resin solution is directly coated at the formation of the film. More specifically, a film can be formed on cloth by means of direct coating. A film is also formed by coating a resin solution over a peel-type sheet and laminated over a cloth. More specifically, a film can be formed over a cloth by means of lamination.

This invention's moisture permeable waterproof cloth is produced by various means. When it is desired to obtain high moisture permeability, a wet-type film forming method by direct coating is used. When productivity is considered, a means of dry-type film forming by direct coating is used. When it is desired to obtain high waterproof properties, a means of dry-type film lamination is used.

In this invention, the above mentioned resins, the ceramic particulate with extreme infrared radiation ability and various solvents are mixed and used.

In the case of the means of dry-type film formation, a polar organic solvent is mixed and used. Dimethyl formamide, dimethyl

acetamide, dimethyl sulfoxide, N-methyl pyrrolidone, hexamethylene phosphene amide, etc. are the polar organic solvents used here. A volatile solvent is also used by the means of dry-type film formation. A ketone group solvent or an aromatic hydrocarbon-type solvent, etc. is the volatile solvent used here. Acetone, methyl ethyl ketone, methyl isobutyl ketone, etc. are used as the ketone group solvent. A toluene and xylene, etc. are used as an aromatic hydrocarbon-type solvent.

In this invention, an isocyanate compound is jointly used in a resin solution by means of direct coating and in a binder by means of lamination, respectively, in order to improve the peeling resistance between the resin film and cloth. 2, 4-tolylene di-isocyanate, diphenyl methane di-isocyanate, hexamethylene isocyanate, etc. are used as the isocyanate compound.

A common means of coating (e.g., a means of coating which uses a knife coater and a comma coater, etc.) is used to coat a resin solution over a fiber cloth by direct coating.

The dry-type film making laminating means coats a resin solution over a filling-type paper by knife over a roll coater, etc. After a dry-type film is made, it is laminated over a fiber cloth by using a polyurethane adhesive agent.

All usable here as the fiber cloth are a polyamide synthetic fiber (e.g., nylon 6 and nylon 66, etc.), a polyester synthetic fiber (which is represented by a polyethylene terephthalate), a poly acrylonitrile synthetic fiber, a polyvinyl alcohol synthetic

fiber, a semi-synthetic fiber (e.g., triacetate, etc.) or woven fabrics, knit fabrics, and unwoven fabrics which are made of blended fabrics, (e.g., nylon 6/cotton, polyethylene terephthalate/cotton, etc.).

This invention conducts a water repellent treatment as a post process. The water repellent agent used here is a commonly known agent (e.g., a paraffin water repellent, a polysiloxane water repellent agent and a fluorine water repellent agent, etc.). The water repellent treatment is conducted by a suitable means (e.g., padding, spraying and coating, etc.).

This invention has the above explained constitution.

[Action]

This invention's moisture retaining waterproof cloth has a resin film which contains a ceramic particulate with extreme infrared radiation ability and which absorbs sun energy and converts it to a heat energy with a 2 - 20 um wave length. It then radiates the once absorbed energy as heat energy through the radiation ability. Simultaneously, it greatly curtails the human body's heat energy from leaking to the outside. In short, it shows excellent heat retention properties.

[Examples]

This invention is further explained below with the accompanying Examples. The performance measurement of the cloth in the Examples is conducted by the following means:

(1) Heat Retention Properties:

The surface temperature of the cloth is measured by a thermo viewer (infrared ray sensor: Nippon Denshi KK) inside of a room with a constant temperature of 20°C, 60% RH by using a 100W white light as the energy source.

(2) Moisture Permeability (degree of moisture permeability):

JIS L-1099 (A - 1 means)

(3) Waterproof properties (water resistive pressure):

JIS L-1096 (Low-water resistive pressure means)

(4) Crumple resistant properties: The number of times for making the resin surface is measured by weighing 1 kg under an abrasion speed of 120 times/min by using a Scott-type crumpling resistant tester.

Example 1:

A taffeta fabric (120 piece/inch warp density and 90 piece/inch woof density) is prepared as a base cloth. A nylon 70 denier/24 filament is for the warp and a nylon 70 denier/34 filament for the woof. After it is refined by normal means and dyed by an acid dye, a calendar process is conducted under the following conditions: 170°C temperature; 30kg/cm pressure and 20m/sec. speed using a calendar processor which provides a mirror surface roller.

Then, 60% of manganese dioxide, 20% of ferric trioxide, 10% of copper oxide and 10% of cobalt oxide are mixed, sintered, and then powdered into a grain degree of 1.0μm. A ceramic particulate is then obtained. This ceramic particulate is used in the

following Prescription 1.

A polyurethane resin solution (30% resin solid portion density) which is shown in the following Prescription 1 is coated with an amount of coating of 100g/m² by using a knife-over-roller coater. The solidification of the resin portion is conducted by dipping and shifting through in a 20°C bath tub. It is then continuously cleaned for 10 minutes in warm water (60°C) and dried.

[Prescription 1]

Crysbone* 8114 100 part
(Polyurethane resin
Dai-Nippon Ink Kagaku Kogyo KK product)

Crysbone* BL - 50 2 part
(Isocyanate compound
Dai-Nippon Ink Kagaku Kogyo KK product)

Crysbone Assister* - SD -7 3 part
Dai-Nippon Ink Kagaku Kogyo KK product)

Di methyl formamide 10 part

Ceramic particulate 8 part

Thereafter, a padding treatment (30% contraction percentage) is conducted over the cloth by using a fluoride water repellent emulsion 5%- aqueous solution of Asahi Guard 710 (Asahi Glass KK product); a heat treatment is conducted for 1 minute at 160°C. This invention's moisture permeable waterproof cloth is then obtained.

[Comparative Example 1]

For comparison with this invention, absolutely the same method as the Example 1 is conducted except an aluminum powder is

used instead of the ceramic particulate of Example 1. A moisture permeable waterproof cloth for comparison is then obtained. A carbon powder is also used instead of the ceramic particulate. However, it was difficult to conduct the mixing preparation of the resin solution and a moisture permeable waterproof cloth for comparison purposes could not be obtained.

The properties of the moisture permeable waterproof clothes of this invention's Example and the Comparative Example are measured and the results are shown in Table 1.

Table 1

	本発明	比較例1
3 保溫性(℃)	27.0	25.5
4 透湿度(g/m ² ·hr)	155	125
5 防水圧(cm)	2000以上	2000以上
6 防熱性(℃)	2000	2000

1... this invention

2... Comparative Example 1

3... heat retention properties

- 4... water resistant pressure
- 5... clump resistant properties (number of times)
- 7... more than

As it is clear from Table 1, this invention's moisture permeable waterproof cloth absorbs light source energy well and does not let such escape when compared with Comparative Example 1's moisture permeable waterproof cloth. The surface temperature of the cloth also rises and it shows good heat retention properties. Simultaneously, there are no problems with regard to water resistant pressure and clump resistant properties.

Example 2:

The manufacture of a poly amino acid urethane resin (hereafter called PAU resin) as a polyurethane resin used in this Example is conducted by the following method.

1970g of polytetramethylene glycol (OH value:56.9) and 504g of 1,6-hexamethylene diisocyanate are reacted at 90°C for 5 hours; a urethan prepolymer (NCO equivalent 2340) having an isocyanate group at the end is obtained. 85g of the obtained urethane prepolymer and 85g of α - methyl - L - glutamate NCA are dissolved in 666g of a mix solvent of dimethyl formamide dioxane (7/3 weight ratio). While stirring, 50g of 2% triethyl amine solution are added to them and reacted at 30°C for 5 hours. A PAU resin solution with 65,000 cps (25°C) rust color emulsion with good fluidity is obtained. This PAU resin is used in the following Prescription 2.

This invention's moisture permeable waterproof cloth is made by the following method using this PAU resin.

First, a calendar process is conducted on plain fabric in absolutely the same manner as in Example 1.

Next, using a zirconium carbide particulate (0.9um grain degree) as the ceramic particulate, a resin solution with resin solid portion density of 23% (which is shown in the following Prescription 2) is coated (70g.m² coating amount) by using a knife-over-roller coater. The solidification of the resin portion is conducted in 20°C warm water. It is continuously cleaned in 60°C warm water for 10 minutes and dried.

[Prescription 2]

PAU resin	100 parts
Crysbone* BL-50 (Isocyanate compound Dai-Nippon Ink Kagaku Kogyo kk product)	2 parts
Crysbone Assister* - DS - 7 (Non-ion surfactant Dai-Nippon Ink Kagaku Kogyo kk product)	3 parts
Dimethyl formamide	10 parts
Zirconium carbide	5 parts

A padding treatment (contraction percentage 30%) is conducted on the above cloth by using 5% Asahi Guard 710 (Asahi Glass kk product) fluoride water repellent emulsion aqueous solution. A heat treatment is then conducted at 160°C for 1 minute. This invention's moisture permeable waterproof cloth is thus obtained.

[Comparative Example 2]

A moisture permeable waterproof cloth for comparison is obtained by using absolutely the same method as this invention's Example except that aluminum powder is used instead of the ceramic particulate in this invention's Example. The properties of this invention's moisture permeable waterproof cloth and that of Comparative Example 2's are measured. The results are shown in Table 2.

Table 2

	本發明	比較例2
保溫性 (r)	27.5	25.0
透濕度 (g/m ² ·hr)	365	365
耐水圧 (mm)	2000以上	2000以上
耐粘性 (回)	1800	1650

- 1... this invention
- 2... Comparative Example 2
- 3... heat retention properties
- 4... moisture permeable degree
- 5... water resistant pressure
- 6... clump resistant properties (number of times)

7... more than

As is clear from Table 2, this invention's moisture permeable waterproof cloth absorbs light source energy well and does not let such escape when compared with Comparative Example 1's moisture permeable waterproof cloth. The surface temperature of the cloth also rises and it shows good heat retention properties. Simultaneously, there are no problems with regard to water resistant pressure and clump resistant properties.

Example 3:

This invention's moisture permeable waterproof cloth is made using Example 2's PAU resin by the following method.

A tricot half of course number 52 piece/inch and wale number 40 piece/inch of polyethylene terephthalate 50 denier/24 filament as the base cloth is prepared for both the front thread and back thread; it is refined by a common method and dyed by dispersion dye.

A 16% resin solid portion density of resin solution which is shown the following Prescription 3 is next coated over a peeled off paper by optionally adjusting the amount of coating so as to reach a dried film thickness as 10um of resin film by a knife-over-roll coater by using 0.6um grain degree of zirconium carbide particulate as the ceramic particulate. It is then dried at 60°C for 3 minutes. After a polyurethane adhesive agent solution (which is shown in the following Prescription 4) is coated over the formed resin film with a 60g/m² coating amount by a knife-

over-roll coater, it is dried at 50°C for 3 minutes. The base cloth is pasted over this and thermo-adhered under conditions of 90°C and 3kg/cm².

[Prescription 3]

PAU resin	100 parts
Dimethyl formamide	10 parts
Methyl ethyl ketone	30 parts
Zirconium carbide	3 parts

[Prescription 4]

Crysbone* N-18	100 parts
(Polymer diol Dai-Nippon Ink Kagaku Kogyo kk product)	
Barnock* DN-950 (Di isocyanate Dai-Nippon Ink Kagaku Kogyo kk product)	10 parts
Accel*T (Catalyst Dai-Nippon Ink Kagaku Kogyo kk product)	3 parts
Dimethyl formamide	10 parts
Toluene	40 parts

The paper is peeled off and a padding treatment (30% contraction percentage) is conducted to the obtained laminated cloth by using a 5% aqueous solution of Asahi Guard 710 of fluoride water repellent agent emulsion. A heat treatment is conducted at 160°C for 1 minute. This invention's moisture

permeable waterproof cloth is thus obtained.

[Comparative Examples 3 and 4]

For purpose of comparison with this invention, moisture permeable waterproof cloth are obtained in absolutely the same manner as this invention's Examples, except that an aluminum powder (Comparative Example 3) and a carbon powder (Comparative Example 4) are used instead of using the ceramic particulate of this invention's Examples.

The properties of the moisture permeable waterproof cloth of this invention and the Comparative Examples 3 and 4 are measured. The results are shown in Table 3.

Table 3

	本発明	比較例3	比較例4
吸水性 (g)	26.5	25.5	26.2
透水性 (g/m ² ·hr)	120	100	95
耐水性 (m)	2000以上	2000以上	2000以上
耐候性 (回)	1500	1500	1300

- 1... this invention
- 2... Comparative Example
- 3... heat retention properties
- 4... moisture permeable degree
- 5... water resistant pressure
- 6... crumple resistant properties (number of times)
- 7... more than

As is clear from Table 3, this invention's moisture permeable waterproof cloth absorbs light source energy well and does not let such escape when compared with the Comparative Example 1's moisture permeable waterproof cloth. The surface temperature of the cloth also rises and it shows good heat retention properties. Simultaneously, there are no problems as to water resistant pressure and clump resistant properties.

Effect of the Invention:

This invention's moisture permeable waterproof cloth has excellent heat retaining properties because it contains a ceramic particulate having extreme infrared radiation ability as well as excellent moisture permeability properties and abrasion resistance.

The moisture permeable waterproof cloth of this invention is a suitable material, especially for sport clothes.

Translator's Note:

***= Phonetic Translation**

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